

## "NO<sub>x</sub>" Formation and Kinetics of "NO<sub>x</sub>" Reduction in Fluidized Bed Combustion of Carbonaceous Materials

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In contrast with the extensive investigations concerning sulfur retention in the United States, the initial stage of development in Japan has focused on the nitric oxide emission control.

The staged air firing is considered to be the most promising method for control. In this operation the fluidized bed is maintained under a deficiency of air and the design factors influencing sulfur retention, formation and destruction of nitric oxide, ammonia and other nitrogenous compounds, and combustion efficiency are complex interactions. The optimum design of a fluidized bed combustor requires sound qualitative information concerning the behavior of nitric oxide formation and quantitative descriptions of the kinetics of "NO" destruction. The objective of this report is to describe the recent findings concerning "NO<sub>x</sub>" formation and the kinetics of "NO<sub>x</sub>" reduction reactions in fluidized bed combustion of carbonaceous materials.

### I. NITRIC OXIDE EMISSION FROM FLUIDIZED BED COMBUSTION

#### Equipment, Procedure and Materials

The combustors are stainless steel vessels, 50mm diam. 580mm long and 76mm diam. 850 mm long. The lower part of the vessel was packed with refractory materials and used for preheating. Fluidizing air or simulated air consisting of oxygen and argon enters the combustor through a multi-orifice plate distributor into a bed of microspherical particles whose chemical and physical properties are given in Table 1. The multi-orifice plate was designed so that a pressure drop sufficient to achieve homogeneous fluidization could be obtained. In a series of experiments carried out to investigate the influence of air staging, the primary stage of the bed was maintained at substoichiometric conditions, while the balance of the air was introduced through the nozzles into the freeboard.

The static bed height was specified to be 10cm. The fluidized bed combustor was externally heated by an electric furnace. The temperature of the bed was controlled by a conventional PID electronic controller.

Feeding of the carbonaceous materials employed was done by means of a solid feeder developed in our laboratory. Thus continuous feed of a small flow rate of solids (such as 0.2 g/min) could be realized. The solids were sent into the fluidized bed combustor at a point 30-35mm above the distributor.

Ash was removed by elutriation and the elutriated solids were removed from the off-gas by a small cyclone separator. In a certain series of experiments, collected solids were used for chemical analysis to obtain the combustion efficiency.

Upstream from the cyclone separator, (5cm below the top cover of the combustor) the off-gas was continuously diverted to a gas-analysis system. A chemiluminescent NO<sub>x</sub> analyzer provided continuous measurement for NO<sub>x</sub> while gas chromatography provided intermittent analysis for H<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>. Known gas mixtures were used to calibrate the gas chromatograph. Kitagawa NH<sub>3</sub> low-range detector tubes were used to analyze NH<sub>3</sub>. the experimental conditions employed are shown in Table 1, while the carbonaceous materials employed for the present series of experiments are shown in Table 2.

Table 1 Scope of experiment

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Inert particles: Microspherical particles	
SiO <sub>2</sub> :8.93%, Al <sub>2</sub> O <sub>3</sub> :90.61%, Fe <sub>2</sub> O <sub>3</sub> : 0.46%	
Surface mean particle diameter of the inert particles:	
580 microns for coal and char, 613 microns and 322 microns for coke	
Bulk density: 0.57 g/cm <sup>3</sup>	
Temperature of fluidized bed: 700-1000°C	
Static height of bed: 10cm	
Diameter of coal and char particles: 500-710 microns	
Mean diameter of coke particles,	
Coke I : 109 microns	
Coke II : 191 microns	
Coke III: 460 microns	
(A)	ID 50mm combustor (height 490mm)
	Flow rate of fluidizing air and
	simulated air: 4.2-8.1 NL/min
	Feed rate of fuel particles: 0.5-1.7 g/min
(B)	ID 76mm combustor (height 850mm)
	Flow rate of fluidizing air and
	simulated air: 3.9-10.4 NL/min
	Feed rate of fuel particles: 0.37-1.27 g/min

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#### The effects of volatile components on nitric oxide emission<sup>4,6)</sup>

Fundamental investigations concerning the effects of stoichiometric ratio and combustion temperature on "NO" emission were carried out by use of various types of carbonaceous materials indicated in Table 2. Typical results are shown in Fig.1 (a) and (b). Figure 1 (a) indicates that a considerably high level of "NO" emission in the presence of reducing gas (H<sub>2</sub>, CO and CH<sub>4</sub>) was observed under a substoichiometric combustion of coal while quite a low level of "NO" emission was detected under a starving combustion of char.

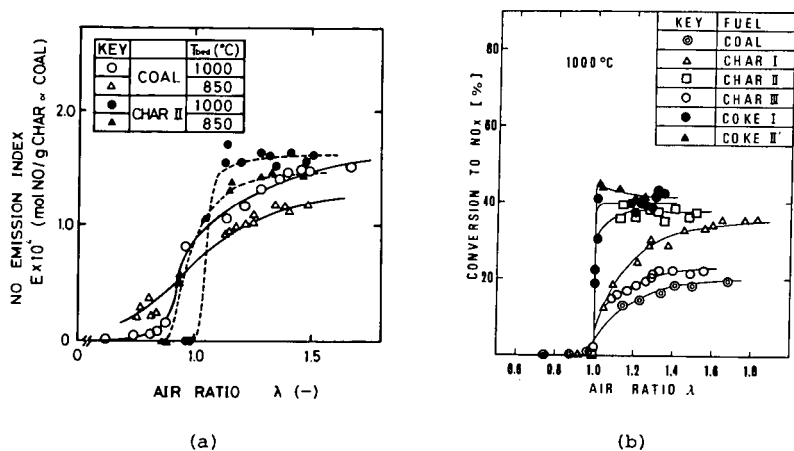


Fig. 1 Effects of stoichiometric ratio and combustion temperature on "NO" emission

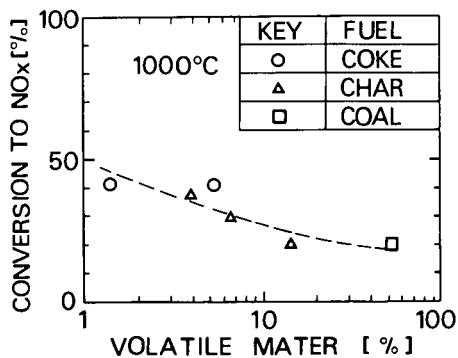


Fig. 2 Conversion of fuel nitrogen to NO with respect to volatile components

Table 2 Proximate and ultimate analyses of carbonaceous materials used

Proximate analysis [wt%]					
		Volatile matter	Fixed-carbon	Ash	Moisture
Char I	*1	3.83	54.09	19.8	22.28
Char II	*2	2.74	66.00	24.47	6.69
Char III	*3	10.89	65.04	19.84	4.32
Coal	*4	43.3	39.1	12.7	4.9
Coke I	*5	1.4	96.0	1.4	1.2
Coke II	*5	3.7	92.5	0.2	3.6
Coke II'	*5	5.3	90.9	0.4	3.4
Coke III	*5	10.9	85.7	1.7	1.7
Carbon	*6	5.2	94.7	0.1	(3.2)

Ultimate analysis [dry%]							
		C	H	N	S	O	Ash
Char I	*1	96.21	0.59	0.54	0.27	3.91	25.48
Char II	*2	71.66	1.03	0.61	0.01	0.34	26.35
Char III	*3	70.99	2.77	1.27	0.02	4.21	20.74
Coal	*4	66.9	5.4	1.4	0.1	13.2	13.0
Coke I	*5	94.0	1.3	0.7	2.7	-	1.3
Coke II	*5	89.2	2.1	1.5	2.9	4.1	0.2
Coke II'	*5	91.7	2.6	2.4	2.1	0.7	0.5
Coke III	*5	87.1	4.0	2.5	1.4	3.2	1.8
Carbon	*6	97.2	1.4	0.1	0.1	1.1	0.1

\*1 Char I: produced from Liddell coal/Australia

\*2 Char II: produced from Taiheiyō coal, pyrolysis temperature: 800°C

\*3 Char III: produced from Taiheiyō coal, pyrolysis temperature: 600°C

\*4 Coal: Taiheiyō coal

\*5 Coke: originated from petroleum residue

\*6 Carbon: activated carbon from petroleum residue

"NO" emission from char or coke, both of which contained less volatiles than coal is radically reduced as the stoichiometric ratio is reduced. This fact together with the reduced ammonia emission suggests that staged air firing may provide advantageous combustion modification for the control of "NO<sub>x</sub>" emission. This is discussed in the forthcoming sections.

Figure 1(b) demonstrates the conversion ratio of fuel nitrogen to fuel NO of various carbonaceous materials. In this experiment the effect of thermal-NO was eliminated by using AR/O<sub>2</sub> mixture instead of air. The level of NO emission under an excess air condition seemed to be considerably dependent on the volatile contents of fuel.

The fraction of fuel bond nitrogen which formed fuel-NO at  $\lambda = 1.3$  is illustrated in Fig.2 where volatile contents were calculated on

ash and moisture free basis. This indicates that the conversion rate of fuel bond nitrogen to nitric oxide was reduced with the increased volatile contents.

Jonke et al.<sup>3)</sup> reported that "NO" emission under a substoichiometric combustion of coal was increased at decreased temperature. This behavior was observed in Fig.1(a). Thus "NO" emission level from high volatile coal at elevated temperatures, approaches the level of "NO" emission from less volatile fuels at lower temperatures. This fact together with the decreased ammonia formation at elevated temperatures suggests also the efficient combustion modification for the reduction of "NO" emission.

#### Formation of nitrogenous compounds and staged combustion<sup>4,5,6)</sup>

A series of experiments were carried out to investigate the influence of air staging. In this operation, the primary stage, which was a fluidized bed, was maintained at substoichiometric conditions while the balance of air, (the secondary air) was introduced through a nozzle into the freeboard. A significant reduction of "NO" emission by staged air firing can only be realized provided the emission of "NO" as well as other nitrogenous compounds from the primary stage are significantly reduced. Thus the ammonia emission from coal and char are measured by the detector tube method. Typical results are shown in Fig. 3. Ammonia emission was not detected under an excess air condition. Under a substoichiometric condition, this could be reduced by elevating the combustion temperature, or reducing moisture, or volatile contents. In the case of char combustion, the ammonia emission under starving combustion at 850°C was approximately 1/7 of the "NO" emission under an excess air condition.

These results suggest that a significant reduction of "NO" emission can be achieved by a staged combustion of char. A preliminary experiment was carried out to evaluate the possibilities of staged air firing. Experimental results indicate that an approximately 90% reduction of "NO" emission was attained in the case of staged combustion of char where this was evaluated on the basis of an "NO" emission index obtained for conventional operations. However, the maximum level of "NO" reduction in this operation for coal remained at 33.5%.

#### Effect of in situ formed carbon on "NO" reduction<sup>1,2,9)</sup>

Carbonaceous materials within the bed were reported to be effective in "NO" destruction. The steady state carbon concentration within the bed was measured. After terminating the feed of fuel solids, the amount of carbon dioxide and monoxide originating from the remaining carbon particles was measured by means of the gas bag method. The results obtained are compared with the level of "NO" emission in Fig. 4. These results indicate that "NO" emission was inversely related to the steady state carbon concentration. Furthermore, the steady state carbon concentration within the bed was found to be considerably small.

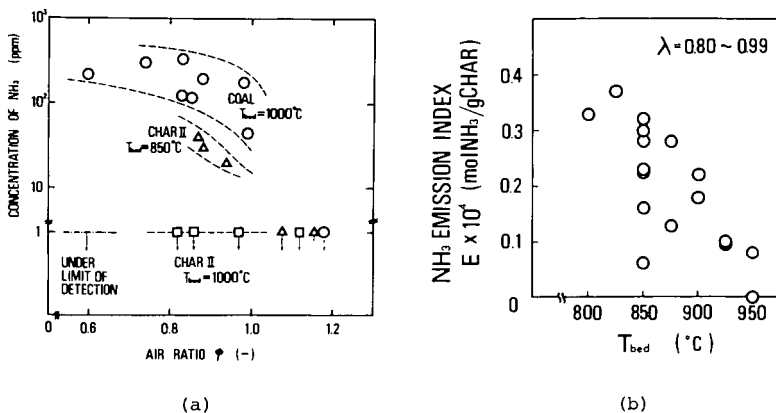


Fig. 3 Emission of ammonia from combustion of coal and char

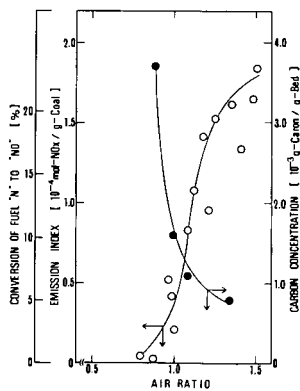


Fig. 4 NO emission decreased with the increase of steady state carbon concentration within the bed

## Intrinsic Ratio of Fuel Nitrogen Conversion to Nitric Oxide

The significant magnitude of nitric oxide destruction by char or other reducing gas suggests that the concentration of nitric oxide measured at the top of the bed or freeboard did not reflect the intrinsic evolution level of nitric oxide from the combustion. Thus the measured value depended on the relative importance of the rate of "NO" formation reaction and the rate of "NO" reduction. The experimentally obtained concentration profiles along the height of the bed and freeboard may verify this mechanism. Information concerning the intrinsic evolution level of "NO" from char particles is required to describe the above process quantitatively. The response curve of "NO" formed within the combustor by the puls input char was measured so that the effect of the subsequent "NO" reduction by char or other reducing gas could be minimized. This is shown schematically in Fig. 5(a). The response peak of "NO" formed by the combustion with the reduced intensity of the input puls tends to a certain value from which the intrinsic ration of fuel nitrogen conversion to nitric oxide could be evaluated. Typical results are illustrated in Fig. 5(b). This value seems to be a little smaller than the value obtained by continuous combustion in a small experimental facility. This fact suggests that the emission level of nitric oxide is affected by the intensity of combustion, consequently the steady state carbon concentration within the bed. However, these results do not reduce the validity of the experimental results obtained by a small scale combustion facility concerning the behavior of nitric oxide emission.

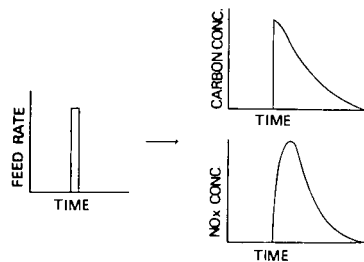
## II. KINETICS OF "NO" DESTRUCTION

### Rate of "NO" reduction by char<sup>7)</sup>

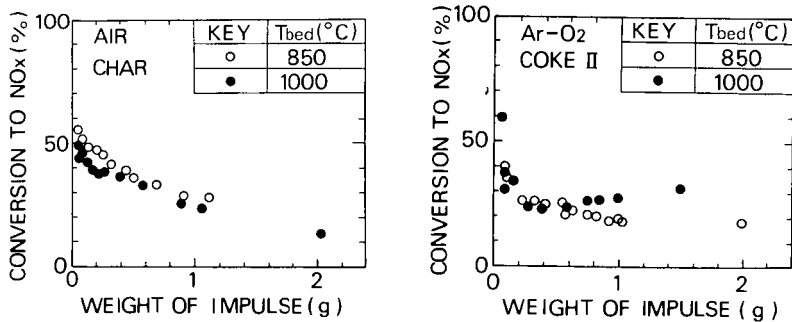
An isothermal fixed bed tubular reactor of diluted char particles and activated carbon (char II, carbon in table 2) was used to measure the reaction rate over a temperature range which is of practical importance in fluidized bed combustion. Since the "NO" concentrations employed in the experiment were of the order of several hundred ppm, the amount of carbon could be assumed to be constant. The details were reported elsewhere.

The reduction of "NO" by char and activated carbon was first order with respect to "NO" concentration. Figure 6 represents the Arrhenius plot for char where  $\alpha$  ( $\alpha$ ) denotes the ratio of the concentration of oxygen to the concentration of "NO" at the inlet. Thus the line corresponding to  $\alpha=0$  indicates this rate.

At lower temperature ranges the activation energy for char was 16.3 kcal/mol and coincided with the data reported previously. Above 680°C the activation energy was 58.6 kcal/mol. The reason for the increase in the activation energy has not been explained. In the lower temperatures the desorption of carbon-oxygen surface complex was considered to control the overall rate. The gaseous reaction product was N<sub>2</sub>, CO and CO<sub>2</sub>. As the temperature was elevated, the fraction of CO in the reaction product increased.



(a)



(b)

Fig. 5 Intrinsic conversion ratio of fuel nitrogen to nitric oxide



# Rate of "NO" reduction by char under an excess air condition<sup>10,11)</sup>

Kinetic information concerning whether or not "NO" can be reduced by char in the presence of oxygen is required in order to analyze the mechanism of "NO" destruction within the bed and freeboard. The use of a fixed bed of diluted char particles was restricted to a range of lower temperatures and lower oxygen concentrations since the char was consumed by combustion reaction. The rate of char combustion is approximately a hundred times faster than the "NO" reduction.

The "NO" destruction accompanied by oxidation of char was also assumed to be first order with respect to "NO" concentrations. This assumption was verified under low oxygen and "NO" concentrations. The results are shown in Fig. 6. The reaction was significantly accelerated by adding oxygen. An increased rate was also observed for "NO" destruction by activated carbon.

Over a range of higher temperatures the effects of the added oxygen on the rate could not be investigated since the carbon concentration

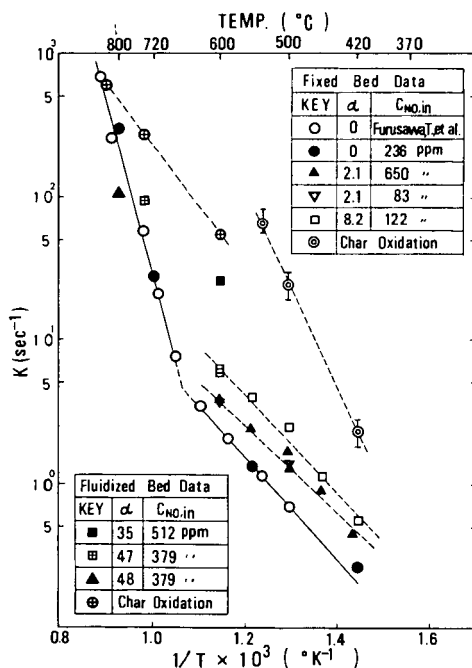


Fig. 6 Rate of NO reduction by char and the effect of oxygen on "NO" reduction

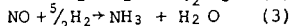
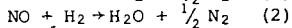
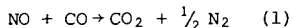
could not be assumed constant. Thus a fluidized bed reactor with a continuous feed and discharge of carbon (150mm height) was used to analyze the rate for higher oxygen concentration; namely, a large value of  $\alpha$  and a higher temperature. Furthermore, the reduction of "NO" in a simulated combustion product containing CO<sub>2</sub> was studied. A remarkable result from these experiments is that a significant reduction of "NO" was realized even under an excess air condition in which oxygen remained in the outlet flow.

The simplified bubbling bed model by Kunii and Levenspiel was used to evaluate the reaction rate in the presence of oxygen. First, the effective bubble diameter was calculated as an adjustable parameter by curvefitting the experimental data obtained in the absence of oxygen to the curve calculated theoretically by the above model and the kinetic data shown previously. Then the increased rate in the presence of oxygen was evaluated by changing the rate, but by keeping the other parameter, including the effective bubble diameter, constant.

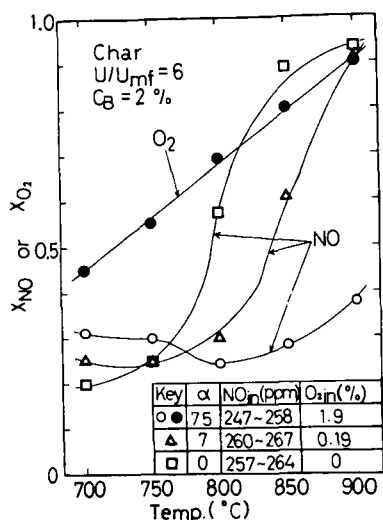
In this evaluation of the rate, the effect of fuel "NO" formed by the simultaneously occurring combustion of char was compensated for. The details are shown elsewhere. The estimated rate is shown in Fig. 5. An increased rate of "NO" reduction was observed in the presence of oxygen at both 600°C and 750°C. The rate was not significantly reduced by the presence of oxygen at 800°C. At 853°C the rate of "NO" destruction was reduced by coexisting oxygen. The extent of "NO" reduction by both char and activated carbon in both the absence and presence of oxygen was measured over a temperature range of 700~900°C where the height of the bed was 150mm. The results together with the extent of oxygen consumption is shown in Fig. 7. The increased rate for char was verified up to approximately 750°C and that for the activated carbon up to 950°C.

#### Reduction of "NO" in the presence of carbon monoxide and hydrogen<sup>8,12)</sup>

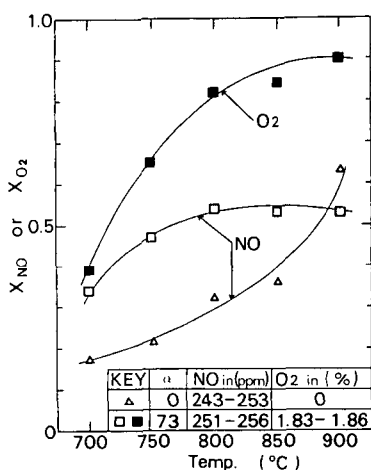
The preliminary investigation concerning the reduction of nitric oxide by char in the presence of hydrogen or carbon monoxide was carried out over a temperature range of 700-800°C in a fixed bed reactor mentioned previously. The reaction was first order with respect to nitric oxide. Ammonia was formed in the nitric oxide hydrogen-char system. The presence of hydrogen and carbon monoxide decreased the consumption of carbon to nearly zero, as:



The rates and activation energies obtained for the above catalytic reactions for (1) or (2) + (3) agreed with the rate of noncatalytic reduction of nitric oxide by char within the experimental error. This strongly suggested that the activated adsorption of nitric oxide on the char surface controlled the overall rates. The ratio of ammonia formed by reaction (3) to the consumed nitric oxide which is found to be constant at each temperature is decreased with an increased temperature.



(a) Char



(b) Carbon

Fig. 7 Increased extent of "NO" reduction caused by oxygen

#### Concluding Remarks

This paper described the recent findings concerning the behavior of "NO<sub>x</sub>" formation in a fluidized bed combustor obtained by use of a variety of carbonaceous materials. The "NO" emission under an excess air condition was decreased with an increase in the volatile contents of fuels. The emission of "NO" and other nitrogenous contents formed under a sub-stoichiometric combustion was also strongly dependent on the volatile contents. The staged combustion of less volatile char and coke provided a radical reduction of "NO" emission. The steady state carbon concentration was measured and "NO" emission was found to be inversely related to the carbon concentration. The intrinsic conversion ratio of fuel nitrogen to "NO" was measured. The kinetics of "NO" destruction by char in both the absence and presence of oxygen was investigated. The rate for char was increased up to 750°C. "NO" was reduced catalytically by carbon monoxide and hydrogen over a char surface, but the rate was not increased.

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#### Literature Cited

- 1) Beér, J.M., A.F. Sarofim, L. Chan & A. Spruce: Proceedings of the 5th Int. Conference on Fluidized Bed Combustion, p577 - p592 (1977)
- 2) Beér, J.M., A.F. Sarofim & Y.Y. Lee, Proceedings of the 6th Int. Conference on Fluidized Bed Combustion, p942 - p955 (1980)
- 3) Jonke, A.A., G.J. Vogel, E.L. Carls et al.: Chem. Eng. Prog. Symp. Series 68, NO 126, 241 (1972)
- 4) Furusawa, T., T. Honda, J. Takano and D. Kunii: J. of Chem. Eng. Japan 11, 377 (1978)
- 5) Furusawa, T., N. Yamada, T. Sendo and D. Kunii: J. of Chem. Eng. Japan 12, 71 (1979)
- 6) Furusawa, T., T. Honda, J. Takano and D. Kunii: Fluidization, Proceedings of 2nd Eng. Found. Conf., Cambridge University Press (1978)
- 7) Furusawa, T., D. Kunii, N. Yamada and A. Oguma: Int. Chem. Eng. 20, 239 (1980) or Kagaku Kogaku Ronbunshu 4, 562 (1978)
- 8) Furusawa, T., D. Kunii and T. Tsunoda: under preparation
- 9) Gibbs, B.M., F.J. Pereira and J.M. Beér: 16th Symposium on Combustion, Cambridge, 461 (1976)
- 10) Kunii, D., K.T. Wu and T. Furusawa: Chem. Eng. Sci. 35, 170 (1980)
- 11) Kunii, D., T. Furusawa and K.T. Wu: ed. J.R. Grace and J.M. Matsen, Fluidization, Plenum Publishing Corp. New York, pl75 - pl83 (1980)
- 12) Cowley, L.T. and P.T. Roberts: Paper submitted for presentation at the Fluidized Combustion Conference, 28-30th Jan. (1981) held at the Energy Research Institute, University of Cape Town, South Africa